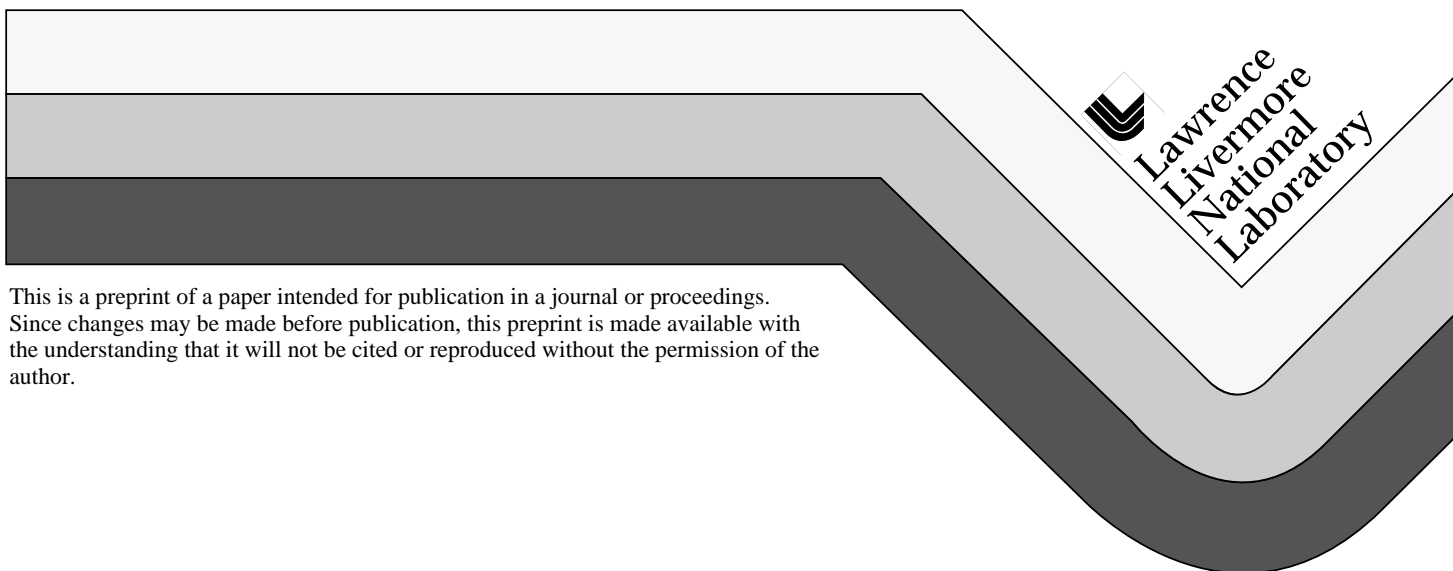


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ANALYSIS OF DISSOLVED BENZENE PLUMES AND METHYL TERTIARY BUTYL ETHER (MTBE) PLUMES IN GROUND WATER AT LEAKING UNDERGROUND FUEL TANK (LUFT) SITES.

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INTRODUCTION

The 1990 Clean Air Act Amendments mandate the addition of oxygenates to gasoline products to abate air pollution. Currently, many areas of the country utilize oxygenated or reformulated fuel containing 15-percent and 11-percent MTBE by volume, respectively. This increased use of MTBE in gasoline products has resulted in accidental point source releases of MTBE containing gasoline products to ground water. Recent studies have shown MTBE to be frequently detected in samples of shallow ground water from urban areas throughout the United States (Squillace *et al.*, 1995). Knowledge of the subsurface fate and transport of MTBE in ground water at LUFT sites and the spatial extent of MTBE plumes is needed to address these releases.

The goal of this research is to utilize data from a large number of LUFT sites to gain insights into the fate, transport, and spatial extent of MTBE plumes. Specific goals include defining the spatial configuration of dissolved MTBE plumes, evaluating plume stability or degradation over time, evaluating the impact of point source releases of MTBE to ground water, and attempting to identify the controlling factors influencing the magnitude and extent of the MTBE plumes. We are examining the relationships between dissolved TPH, BTEX, and MTBE plumes at LUFT sites using parallel approaches of best professional judgment and a computer-aided plume model fitting procedure to determine plume parameters. Here we present our initial results comparing dissolved benzene and MTBE plumes lengths, the statistical significance of these results, and configuration of benzene and MTBE plumes at individual LUFT sites.

MATERIALS AND METHODS

To determine the fate and transport of dissolved MTBE plumes, we have reviewed LUFT ground water data submitted to us by several oil companies, including ARCO, BP, Shell, Chevron, and Unocal. We have examined the relationship between TPH, MTBE, and benzene concentrations in individual monitoring wells for 245 LUFT sites (total of 1,858 monitoring wells) in 24 counties in California, and we have defined spatial extent of the dissolved Total Petroleum Hydrocarbon (TPH), MTBE, and benzene plumes at 30 California LUFT sites.

Dissolved TPH, benzene, and MTBE plumes sites were plotted by hand using our best professional judgment in conjunction with California State Water Quality Control Board (SWQCB) hydrogeologists. All sites met the following criteria: (a) have 8 or more sampled wells (b) reported analytical results for TPH, benzene, and MTBE on the same date and (c) were included in the LLNL/UC California LUFT historical Case Analysis (Rice *et al.*, 1995) and therefore had accessible digitized map coordinates. Of the 30 sites analyzed, the median number of wells per site was 10.5 (max= 22). The ground water data analyzed represented data from one quarterly sampling during 1995.

Site maps were generated that contained all well names and well locations. Each site was individually scaled to produce maps of equal absolute size. Individual maps displaying measured concentrations of TPH, benzene, and MTBE were produced for initial data evaluation and plume estimation. Ground water elevation data was used to generate estimates of gradient magnitude and direction. Values were produced by a two-dimensional least squares fit of a plane surface through elevation data points from each individual sampling period. Time series results of gradient direction, magnitude, number of wells sampled, and R-squared value characterizing the plane fit were analyzed. Anomalous behavior indicative of active remediation in the ground water gradient data was used as a screening tool to eliminate sites that appeared to have undergone pump-and-treat remediation.

In order to compare MTBE and benzene concentrations of similar regulatory significance, we have evaluated benzene plumes at 1 ug/L, the California maximum concentration limit, and evaluated MTBE plumes at 20 and 200 ug/L, the concentration levels considered in the USEPA 1992 draft Health Advisory. Estimated plume lengths were calculated by measuring from the well containing the highest TPH concentration to the furthest margin of the contour of interest. Exceptions to this method were made when the highest benzene and MTBE concentration occurred at a well that differed from the well with the highest TPH value, and when the MTBE plume was clearly separate from the benzene and TPH plumes. The margin of the 1 ug/L benzene contour was defined by monitoring wells with benzene concentrations at or near the limit of detection (0.5 ug/L). The boundaries of the 20 and 200 ug/L MTBE contours were determined by the positions of monitoring wells with MTBE concentrations near these values or by assuming an exponential decrease in concentrations to boundary wells. In some cases, benzene or MTBE data was inadequate to define plume lengths.

RESULTS and DISCUSSION

We have evaluated the correlation of the relationship between concentrations of TPH, benzene and MTBE in ground water samples in each of 1,858 monitoring wells at 245 California LUFT sites. This analysis demonstrates that among these parameters, benzene and TPH show the strongest correlation ($\rho = 0.715$), yet variations extend over two orders of magnitude. Correlation between benzene and TPH concentrations in individual monitoring wells observed in this study were compared to those generated from a much larger data set obtained in the LLNL/UC California LUFT Historical Case Analysis (Rice et al., 1995) and show nearly identical distributions, supporting conclusions from the smaller data set used here.

MTBE and TPH concentrations show extremely weak correlation ($\rho = 0.276$), with variations extending over three orders of magnitude. Benzene and MTBE concentrations show no significant correlation, with variation ranging over as much as five orders of magnitude ($\rho = 0.122$). These results show that MTBE concentrations in a given monitoring well cannot be predicted from benzene and TPH concentrations. Several important factors such as site release history, differences in the physical properties, and biodegradation rates for benzene and MTBE are presumed to account for the lack of correlation between benzene and MTBE concentration values.

Dissolved TPH, benzene, and MTBE ground water plumes were defined for 30 California LUFT sites. In general, hand drawn contours for dissolved TPH, benzene, and MTBE plumes parallel the relationships observed between benzene, TPH, and MTBE concentrations in monitoring wells at 245 sites. Benzene plume contours closely resemble the overall shape of TPH plume contours, while the overall shape and location of MTBE plumes shows greater variation. In addition, in several cases the areas of highest MTBE concentrations "hotspots" do not overlap or co-locate with the benzene and TPH plumes. The locations of past and present underground storage tanks suggest that multiple releases at these sites account for the separate MTBE and benzene/TPH plumes.

Plume lengths for benzene at 1 ug/L were determined for 23 sites. There was inadequate data to define plume length at 6 sites and 1 site had a dissipated benzene plume (<0.5 ug/L). Among this dataset, we found that 87% of the 1 ug/L benzene plumes extend less than 300 ft. The distribution of these 23 benzene plume lengths is nearly identical to the distribution of the benzene plume lengths calculated using a Gaussian exponential model to fit benzene concentration data for 271 LUFT sites in the LLNL/UC California LUFT Historical Case Analysis (Rice et al., 1995). The distribution of benzene plume lengths generated in this study also agrees well with the distribution of benzene plume lengths estimated by Buscheck et al. (1996) for 62 Chevron LUFT sites. The Chevron study measured benzene plume length as the distance from the edge of the contaminant source (area defined as the edge of non-aqueous phase liquid or residually saturated soil) to a downgradient monitoring well at or near the detection limit. Overall, the close agreement of the cumulative distributions of benzene plume lengths for all three studies is especially significant given the different methods used to estimate benzene plume length.

Plume lengths for MTBE were determined for 19 sites at 200 ug/L and for 18 sites at 20 ug/L concentrations. Remaining sites lacked information to define plume length for two reasons. First, in many cases, MTBE detection limits were very large, due to the dilution utilized to measure BTEX concentrations present in the ground water sample. Second, because the extent and location of the MTBE and benzene plumes vary, monitoring wells installed to define the benzene plume in some cases failed to

delineate the MTBE plume. Within this dataset, we found that 83% of both the 20 ug/L MTBE and the 200 ug/L plumes extend less than 300 ft. Future work will focus on examining the distribution of MTBE plume lengths over time at LUFT sites. Many MTBE plumes may still be "growing" since MTBE has only recently been used in large quantities. In contrast, studies indicate that the vast majority of benzene plumes are stable or shrinking (Rice et al., 1995, Buscheck et al. 1996).

Although generalizations are limited by the small number of MTBE plumes in this study, our initial plume length probability distribution is best fit by the two-parameter Frechet (Type II extreme value) distribution. The fit parameters (least squares fit) are ($u=116, k=1.8$), ($u=102, k=2.2$), and ($u=80, k=2.1$) for 1 ug/L benzene, 20 and 200 ug/L MTBE respectively. The respective levels of significance by the Kolmogorov-Smirnov goodness of fit test are 0.82, 0.89, and 0.71. Analysis of a larger number of sites will be performed to further evaluate the significance of fit to the two-parameter Frechet distribution. Given these distributions, larger parent cumulative distributions can be predicted. The fitted distribution indicates that the present population of MTBE plume lengths are statistically smaller than population of benzene plumes at the concentration levels considered. 85% of benzene plumes, 92% of 20 ug/L and 95% of 200 ug/L MTBE plumes are less than three hundred feet. Additional time series data is required to evaluate whether MTBE plumes increase, stabilize or degrade over time.

MTBE and benzene plume lengths from individual sites were compared to obtain a relative measure of the degree of MTBE migration as compared to benzene at these LUFT sites. While MTBE plumes at an individual LUFT site display a general increasing trend with benzene, a great deal of variability exists. Examination of relative plume lengths (MTBE plume length divided by corresponding benzene plume length at each site) shows that for 50% of the sites the relative length is less than one, and 33% of the sites the relative length is greater than one (for 17% of the sites no MTBE plume length was measurable due to very low concentration levels or sparsity of data). Therefore, at an individual site, the lengths of 20 ug/L MTBE plumes in this study vary from approximately half to three and a half times the length of 1 ug/L benzene plumes. These results clearly show that benzene and MTBE plume lengths are not well correlated on a site by site basis. Therefore, MTBE plume length cannot be predicted from benzene plume length at LUFT sites. The release history may be the most important factor in determining the relative degree of migration of MTBE versus benzene at a LUFT site, since for a single release scenario the resulting MTBE plume is expected to migrate further from the release point than the benzene plume due to differential retardation and preferential biodegradation. This has been demonstrated *in situ* for a controlled release at the Borden Aquifer Site (Poulsen et al., 1992). In contrast, our plume analysis at LUFT sites where multiple or chronic long term releases may have occurred show that MTBE plume lengths are unpredictable as compared to benzene plume lengths.

CONCLUSIONS

The results of this study show that there is extensive variation between dissolved MTBE plumes and benzene plumes at existent LUFT sites. First, MTBE concentrations in a given monitoring well cannot be predicted from benzene and TPH concentrations. Second, benzene and MTBE plume lengths are not well correlated on a site by site basis. MTBE plumes in this study at 20 ug/L vary from approximately 0.5 to 3.5 times the length of benzene plumes at 1 ug/L. Among the LUFT sites in this study, MTBE plume lengths cannot be predicted from benzene plume lengths.

The benzene plume lengths measured in this study support previous findings (Rice et al., 1995; Buscheck et al., 1996) indicating that a majority of plumes extend less than 300 ft. This study further indicates that the present population of MTBE plumes are statistically shorter than benzene plumes. Future work will evaluate increases, stabilization or degradation of MTBE plumes over time.

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